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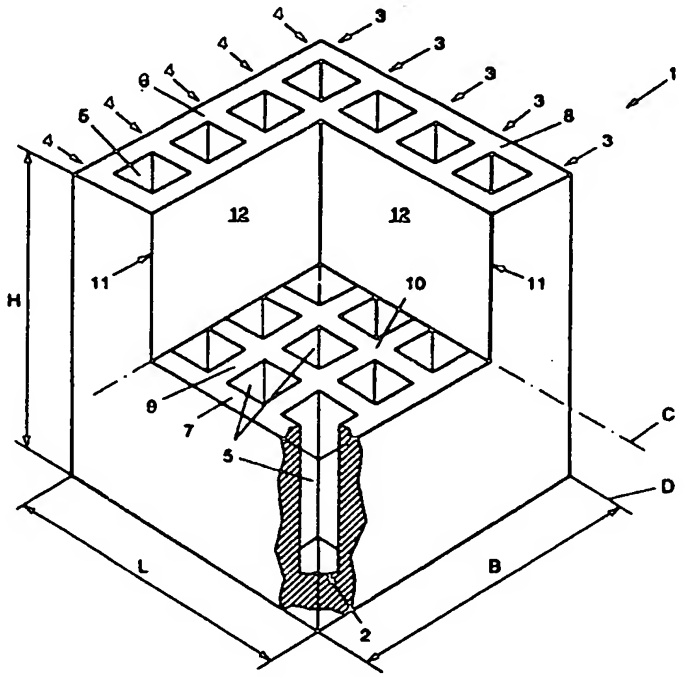
(57) Abstract

A method for manufacturing biodegradable products with a blown foamy structure, wherein a mass comprising at least natural polymers such as starch is passed under pressure into or through a mould (23, 63) and the mass (M, S) is heated in the mould (23, 63) in a manner such as to give rise to at least cross-linking of natural polymers, while the mass prior to the introduction into the mould has a temperature which is below the gelatinization temperature and in the mould is brought at least to the baking temperature.



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Title: Process and apparatus for manufacturing biodegradable products, and biodegradable products

The invention relates to a method for manufacturing biodegradable products, to an apparatus which can be used therefor and to products obtainable according to this method. The products to be manufactured according to the invention have a foamy structure. More particularly, the foamy material always comprises at least three parts: two relatively dense layers on the outside, which, as it were, form a skin, and between them a foam structure as core. The dense layers are firm and strong and consist of substantially closed, small cells. The foam structure of the core is generally open, which means that the cells have burst to allow the gasses evolving during the manufacture, for instance water vapour or carbon dioxide gas, to escape. The cells generally have a firm and solid cell wall due to the relatively high pressure and temperature during the process.

In this description, "gelatinization" is understood to mean a change of a natural polymer from a slightly or completely loose granular or comparable granulate form into a cohesive form which may or may not be dry and/or foamed, in which stretched polymers are present which are mutually bonded to a limited extent, if at all. That is to say, a transition occurs from a solid substance, a colloidal solution or suspension to a more homogeneous fluid mass. Depending on the polymers used, "gelatinization" should therefore be understood to include, for instance, gelling, gellating and the like.

In foamed products where only gelatinization occurs, as a result of gas evolution, bubbles are formed in the mass to be foamed, substantially after gelatinization. This process occurs at relatively low temperatures and pressures. Over the entire cross section, such products have approximately the same structure of relatively small cells with walls of substantially uncross-linked natural polymers.

In this description, "baking" is understood to mean a method in which both gelatinization and cross-linking occur, at relatively high temperature and/or pressure. As a result, the formation of gas arises relatively soon, so that bubbles are already formed prior to or during gelatinization. As a result of *inter alia* the high pressure adjacent strongly heated parts, the polymers cross-link quickly when using a mould or like baking form with a temperature at or above the baking temperature.

These baked products have a core with relatively large cells, enclosed between skin parts with relatively small cells. The cell walls have a relatively high density and the natural polymers included therein are cross-linked to a high extent, which means that they have entered into mutual chain bonds. Such a baked product therefore has a sandwich-like structure.

International patent application 91/12186 discloses a method for manufacturing biodegradable products by heating in a baking mould a batter which comprises at least natural polymers in the form of starch or derivatives thereof. The batter is introduced into an open platen set, for instance a wafer iron, whereafter the platen set is closed and the batter is "baked". This results in a thin-walled product which is biodegradable and

yet firm and is relatively well resistant to moisture, at least as long as the skin of the product is not damaged. The product is ready immediately and so requires no post-treatment. Owing to the heating to relatively high temperatures, a structure of blown cells and cross-linked starch is created in the product. The products are relatively cheap to manufacture, have good storing properties under different conditions, are light and convenient in use and, owing to their biodegradability, are environment-friendly.

A disadvantage of the use of platen sets is that the batter is introduced into an open mould which is subsequently closed and, for instance, is passed through a continuous oven, where it is heated, for instance by gas burners. Energetically speaking, this is little efficient and moreover the temperature in the baking mould is not properly controllable and may vary strongly during the baking process, which is not beneficial to the quality of the products. Moreover, the products which are obtained according to this method are not particularly dimensionally stable and allow no or only very slight differences in wall thickness, because otherwise no homogeneous structure can be obtained. A further disadvantage of this method is that the introduction of the batter and the removal of the product is very laborious and will often lead to failure in the production. Moreover, with this method no products can be manufactured that are non-withdrawable, so that the moulding freedom is limited.

European patent application 0 512 589 discloses a method for making thin-walled biodegradable products, in which likewise

use is made of platen sets. In this known method, a starch-containing dough is introduced into an open mould cavity in one of the platens, whereafter the platen set is closed and is subsequently heated to a temperature at which only gelatinization occurs but at which the dough is not "baked". The temperature is therefore kept relatively low with respect to the previously described method. With this method, products are obtained which are directly ready for use, that is, they do not require any post-treatment. It is true of the products obtained by this procedure too that they have little dimensional stability and permit no, or only very slight, differences in wall thickness in order to preserve a homogeneous structure. Since the products are not "baked", they are less stiff and exhibit relatively poor resistance to, for instance, water and varying temperature conditions. Moreover, it is true of this method too that filling the platen sets and removing the products is cumbersome and time-consuming, that the products can easily be damaged when being removed and cannot be non-withdrawable, so that the freedom in the moulding design is limited.

International patent application 93/08014 discloses a method for manufacturing biodegradable products, in which the products are manufactured by extrusion of a mixture comprising at least starch or derivatives thereof. In this method, a dry, crude starch with less than 30% water is mixed with mild acid, which mixture is stirred with a carbonate which, through reaction with the acid, can give rise to CO_2 gas. This mixture is introduced into an extrusion tank and mixed with water, while

being pressurized and heated to such an extent as to give rise to gelatinization of the starch. In the extrusion tank the acid is reacted with the gelatinized starch, in such a manner that the average molecular weight thereof decreases and the uniform bonds of the starch chains are broken, while moreover, through reaction with the carbonate, CO_2 gas is produced for blowing up the modified starch. The thus obtained mixture of blown starch with altered (micro)structure is thereafter forced through an extrusion die, whereby under the influence of the CO_2 gas a closed-cell structure is obtained with a density of less than 0.032 g per cubic centimeter. Owing to this structure, the thus obtained product has elastic properties and allows of rapid biological decomposition.

A disadvantage of this known method is that the raw materials are to be supplied in relatively dry form and in the extrusion tank are to be mixed with water under simultaneous increase of the temperature in the tank, whereby the desired gelatinization occurs. To that end, the mixture must be heated, which is difficult to effect homogeneously in view of the relatively large mass. As a consequence, the process is relatively poorly controllable. A further disadvantage is that the products obtained in this way have only limited durability and are not water-resistant and moreover are not particularly dimensionally stable. As a result of the extrusion process and the strong expansion occurring after the extrusion, the freedom of design in this method is limited.

European patent application 0 118 240 discloses a method for manufacturing biodegradable medicament capsules and like

products by injection-moulding from a starch composite. To that end, a starch mixture with a low water content is introduced into a closed space, in particular the hopper of an injection-moulding machine, where plasticization of the mixture is provided for at a suitable specific temperature, pressure and humidity. The temperature and pressure are increased to such an extent that the mixture is adjusted to above the vitrification point. Thereafter the plasticized mixture is forced into a cold mould and maintained under pressure, until the or each product has cooled off sufficiently, whereafter the mould is opened and emptied.

The advantage of this known method is that dimensionally stable biodegradable products can be manufactured relatively fast. However, the possible dimensions of products that can be manufactured with this method are limited, owing to the flow path in the mould. In fact, the plasticized mass forced into the mould is cooled directly, which gives rise to solidification and prevents flow of the mass relatively soon after entry of the mould. Moreover, no cross-linking of the starch in the mass occurs, so that the products have relatively weak strength properties and exhibit relatively poor resistance to water and moist conditions in general. In a moist environment the products will take up a great deal of water and thereby become slack; conversely, in a dry environment moisture will evaporate from the products, so that they become hard and brittle. The products obtained with this method have a high density and have no foamy structure.

European patent application 0 407 350 proposes an improved composition of starch composites for use in *inter alia* a method according to the above-described European patent application 0 118 240, by which, for instance through casting or extrusion, products can be manufactured with better strength properties and better resistance to different conditions, in particular as regards humidity and temperatures. To that end, to the composite of starch, a thermoplastic plastic is added, whereafter the mixture is transformed under very well regulated and controlled conditions into a melt allowing subsequent casting or extrusion. By controlling the conditions, it can be ensured that the thermoplastic plastic melts and mixes with the starch without the starch disintegrating.

An advantage of this known method is that the products are dimensionally stable, have good strength properties and exhibit relatively good resistance to humidity and temperature fluctuations. One of the disadvantages of this known method is that the thermoplastic plastic must be added. This reduces the biodegradability and it is less attractive from an environmental point of view. Further, these products too have a relatively high density. Moreover, when using the composite for injection moulding, the above-mentioned drawbacks remain, such as, for instance, the laborious and costly preparation of the composite, the limited possibilities as regards dimensioning and the absence of cross-linking of the natural polymers.

International patent application 95/04104 discloses a method for manufacturing foamed, biodegradable products from starch-containing raw materials, in which an amount of starch is

liquefied in a pre-stage by heating to a temperature far above the gelatinization temperature, whereafter an amount of water-saturated ramie fibres is admixed. This mixture is thereafter passed into or through a mould or converted to a dry granulate. Upon heating of the mixture, the water is to escape from the ramie fibres and to function as blowing agent. When using this known method, a substantially dry granulate of starch is to be strongly heated in the pre-stage, which granulate therefore cannot form a liquid batter. Accordingly, this method suffers from the above-mentioned disadvantages of the gelatinization of the mass prior to its introduction into the mould.

International patent application 92/13004 discloses a method for manufacturing solid and foamed, biodegradable products from starch-containing raw materials. In this apparatus, an amount of moist (20% water) starch is mixed with *inter alia* some water and mixed in a heated vat in order to obtain gelatinization of the mass, whereafter it is processed through an outlet opening into film or sheet. Thereupon, the film can be deformed into, for instance, dish products. In this known method too, the liquidity of the suspension to be processed is obtained by heating the mass to above the vitrification temperature prior to the definitive processing. Moreover, to the heated mass an amount of steam or alcohol vapour is added. The processing means (for instance rollers) are maintained at a relatively low temperature (70°C).

Further, European patent application 0 634 261 discloses a method for manufacturing biodegradable products utilizing a kind of injection-moulding technique, which starts from a mixture of

a first and second biodegradable starting material. The first has a melting temperature of above 100°C, the second of less than 100°C. Either a substance which contains water is added to the starting material, or water is incorporated in the starting material, in such a manner that it can provide for the blowing of the cells. In an extruder press, the mass is heated to above the gelatinization temperature of at least the first starting material, mixed and pressurized and subsequently sprayed into a mould cavity provided in a pressurized space. After introduction of the mass, the pressure is removed, so that the water in the mass expands, blows the cells and exits through the permeable wall of the mould cavity. Such a method requires a complicated composition of starting materials, which moreover are not entirely biodegradable. Further, this known method has the above-mentioned disadvantages resulting from the gelatinization of at least a part of the mass prior to its introduction into the mould. In particular, as a result of *inter alia* the porous walls, the outer wall portions of the products manufactured according to this method will not have a dense, compact wall but a uniform distribution of cells of uniform size throughout the product thickness.

The object of the invention is to provide a method for manufacturing biodegradable products, in which the supply of the starting material is simple, in which the manufactured products are simple to remove from the mould, which allows a relatively great freedom in design and whereby the manufactured products have a good dimensional stability and exhibit relatively good resistance to different conditions, including moist environments

and temperature fluctuations. In particular, the invention relates to a method for manufacturing biodegradable products with a blown, foamy structure, wherein a mass comprising at least natural polymers such as starch is passed under pressure into or through a mould and the mass is heated in the mould, in a manner such as to give rise to gelatinization and cross-linking of the natural polymers, while the mass prior to the introduction into the mould has a temperature which is below the gelatinization temperature and in the mould is maintained at least for some time at a temperature which is above the gelatinization temperature.

Owing to the supply of the mass from which the or each product is to be formed at a temperature which is below the gelatinization temperature, the supply of the mass can be realized in a simple manner, for instance via pumps and pipes. Moreover, a stock of the mass can be priorly prepared and be fed to a processing apparatus directly from a storage tank. By subsequently passing the mass under pressure into or through the mould and only heating it in the mould, it is ensured that the mould is always filled sufficiently. The flow path, that is, the or each path traversed by the mass to and in the mould can then be long to very long with respect to the cross sections of the passages. Only in the mould, first gelatinization of the natural polymers occurs and then cross-linking of those polymers.

Due to the cross-linking that occurs, a firm product is obtained. A natural polymer provides for a relatively firm skeleton which extends around preferably continuous cells that form in the mould due to moisture or other blowing agents which,

as a result of the heat in the mould and the pressure therein, attempt to escape from the mass and thereby form bubbles. As a result, the product obtained has a blown foamy structure. Since the natural polymer provides for a relatively stiff jacket, the thus obtained product is dimensionally stable upon exiting from the mould. Depending *inter alia* on the extent of cross-linkage, the product obtained is more or less flexible.

Since the mould is heated and not the mass prior to being forced into the mould, the temperatures in the mould can be properly controlled, both for the mould as a whole and for each separate portion thereof. As a result, products can be manufactured with different and varying wall thicknesses and with different mechanical properties. In fact, by heating more or less and/or for a longer or shorter period and adjusting, for instance, the pressure, for instance the extent of cross-linkage of the polymers can be controlled locally, so that the mechanical and physical properties are influenced. All this can be simply determined by those skilled in the art.

In an advantageous embodiment, a method according to the invention is further characterized by the features according to claim 2.

By controlling the process conditions, in particular the feed rate of the mass, the temperature of the mould and the pressure in the mould, a product is manufactured in which the cells are smaller adjacent the mould wall than centrally between the walls of the mould. In other words, in the product the cell size increases from the inside to the outside. Thus, a relatively closed, water-tight skin is obtained which properly

protects the product from premature decline, while the inside of the product comprises relatively large cells which can keep the product light and flexible. A further advantage of the skin with a relative large density is that, as a result, a taut and smooth surface is obtained which affords the product an agreeable appearance, has a pleasant feel, is simply removable from the mould, is simply printable and moreover hygienic. Accordingly, in contrast with the known methods, a cell structure is obtained which is non-homogeneous, at least viewed across the wall thicknesses.

In a further advantageous embodiment, a method according to the invention is characterized by the features according to claim 3.

By building up the products according to the invention from dish or sheet parts each having at least one slight thickness with regard to the other dimensions, at least with regard to outside dimensions, voluminous products can be manufactured which can yet be supplied at all points with so much heat during the preparation that the desired extent of cross-linkage occurs. Thus, dish-shaped products can be manufactured, that is, also block-shaped products, with, for instance, a recess in which a product to be packaged can be wholly or partly received, and filler blocks for, for instance, packages, can be manufactured. Also, for instance through extrusion, for instance hollow or finned profiles can be manufactured. A further advantage of the relatively thin sheet parts is that, as a result, a relatively great flexibility is obtained while the products yet maintain the desired strength properties and volumes.

In a first preferred embodiment, a method according to the invention is characterized by the features according to claim 4.

By making use of a batter which is liquid below the gelatinization temperature, preferably at room temperature, supply of the batter can be realized in a simple manner, for instance via pipes and using simple pumping means. Moreover, a stock of the batter can be priorly prepared and be fed to a processing apparatus directly from a storage tank. In this connection, the liquidity of the batter provides the advantage that the flow path in the mould is particularly long. The water in the batter functions as blowing agent and moreover, upon evaporating from the mould, provides space for the expansion of the cells.

The batter preferably consists entirely of biodegradable constituents, in particular in the form of a suspension. As a result, good flow properties of the batter are maintained and crude starting material such as starch can be used, for instance potato starch or tapioca. Moreover, such a suspension can be simply stored, at least better than a mixture already gelatinized.

In Dutch patent application 9300102, incorporated herein by reference, a number of examples of such batters are described. These batters comprise 500 - 1500 parts by weight of starch or starch derivatives, 0.5 - 50 parts by weight of xanthan gum, 5 - 250 parts by weight of a reactive siloxane and 25 - 300 parts by weight of an inert filler in water. Additionally, preferably 0.5 - 50 parts by weight of a salt are further included. However, the embodiments described should not be construed as limitative

in this respect. When other batter compositions are used, the processing conditions, such as pressure, temperature and time, will often have to be adjusted.

Mentioned as suitable natural polymers are native starch, for instance potato starch, maize starch, wheat starch, waxy maize starch, tapioca starch, pea starch, high-amylose starch or rice starch. Preferably, however, potato starch is used, whose amolypectin content can vary between 75 and 100%. Starch derivatives can also be used, for instance, starch which has been modified by etherification, esterification, acid hydrolysis, oxidation, cross-linking and/or the action of enzymes.

In an alternative embodiment, a method according to the invention is characterized by the features according to claim 7 or 8.

The use of relatively dry, optionally slightly prefoamed starting material provides the advantage that relatively little water or other moisture needs to evaporate in the mould, which has appreciable energetic advantages, the more so since the mass only needs to be heated in the mould, not in the pre-stage. The mass can for instance consist of granulate material, in particular more or less spherical particles having small to very small dimensions with respect to the passage openings to and in the mould. This granulate material can contain a blowing agent, for instance in the form of water or blowing agents simply released and/or evaporating upon heating, such as bicarbonates, which provide for gas evolution through decomposition at elevated temperature.

As starting materials, for instance, the natural polymers mentioned in respect of the batter can be used.

In a further advantageous embodiment, a method according to the invention is characterized in that as mould an injection mould is used.

By making use of an injection mould in a method according to the invention, products can be manufactured with both regular and irregular shapes, which are dimensionally stable and can have varying wall thicknesses. Products manufactured in this manner can, for instance, be used as sheet and dish parts, trays and boxes and like dish-shaped packages and as filler for, for instance, packaging products in boxes and the like. One of the important advantages that can be achieved with this method is that a greater freedom in design is obtained than when platen sets are used. The products can be manufactured in withdrawable as well as non-withdrawable manner, since divisible cores and the like can be readily utilized. As a result, for instance undercuts can be integrally moulded. Moreover, greater differences in height can be incorporated in the product in that the flow path can be longer and gravity has no influence, at least no appreciable influence, on the distribution of the mass.

In a further advantageous embodiment, a method according to the invention is characterized in that an extrusion die is used. When using an extrusion die in a method according to the invention, biodegradable sections and the like can be manufactured in a simple manner with the above-mentioned advantages of the cross-linked structure of the natural polymers. Owing to the mass being supplied in cold, preferably

liquid form, the preparation thereof is particularly simple and products with the desired properties can be manufactured in substantially one processing pass. In this manner, for instance, sheets and sections can be extruded which are used in great lengths or can be divided up and, for instance, be used as loose filler in the packaging of products in boxes, crates, bags and the like. Extrusion and the use of an extrusion die should herein be understood to mean in particular forcing a moulding mass under pressure through a relatively small orifice, this orifice determining substantially at least one cross section of the product. The delivery pressure can, for instance, be generated with a pump or a plunger.

Products that are manufactured with a method according to the invention can in a general sense be designed light with respect to the volume, have sufficient strength and elasticity and are properly resistant to different conditions, in particular when using a "skin" with a relatively high density and a core with a relatively low density.

During the manufacture of the products according to the invention, gas formation through evaporation of water or under the influence of blowing agents occurs so fast that foaming occurs concurrently with or preferably prior to the gelatinization. At elevated pressure and/or temperature this effect is achieved, while further more solid material is "compressed" as cell wall. This not only yields a core made up of large cells with firm cell walls but also skin layers with a higher degree of densification of firm small cells.

In addition, there may be a number of other conditions that must be met to obtain the desired result.

The colloidal particles and corresponding conditions must meet requirements to provide for the formation of foam, which requires, among other things, a particular load and particular surface tensions, in conjunction with an internal and external pressure in the foam bubbles.

The charging of the mould cavity must be complete within a very short time, which entails requirements for the "flow" properties and the thrust: during this short period the "flow" properties must remain sufficient to ensure complete filling, while the driving force, the propellant or "foam" gas, must remain present in a sufficient amount to advance the mass (which is increasingly hard to move). Flow should herein be understood to include both the flow of a liquid, such as the liquid batter, and the flow of a granulate-form, relatively dry substance such as small rolling and sliding granules or powder, whether or not in slightly prefoamed form. Accordingly, the length of the flow path is at least dependent on the liquidity of the starting material and, given equal conditions, will be greater for a liquid or suspension than for granulate material. Moreover, the length of the flow path will be positively influenced by a greater difference between the low supply temperature and the temperature of the mould during the baking.

The invention further relates to apparatuses suitable for use in a method according to the invention.

The invention moreover relates to biodegradable products manufactured with a method and/or in an apparatus according to the invention.

To clarify the invention, exemplary embodiments will be described with reference to the drawing.

Fig. 1 shows a biodegradable product, in particular a filler block, manufactured by injection moulding, in perspective view with a part broken away;

Fig. 1a shows, on an enlarged scale, twice a cross section of a wall of a product according to Fig. 1;

Fig. 2 schematically shows in cross-sectional view an injection-moulding apparatus according to the invention;

Fig. 2a shows on an enlarged scale a part of a mould, with mould cavity, in cross-sectional view;

Fig. 3 shows a biodegradable product, in particular an insert tray for a storage box, manufactured by injection moulding, in cross section;

Fig. 4 shows a biodegradable product manufactured by extrusion, in perspective view; and

Fig. 5 schematically shows in cross-sectional view an extrusion apparatus according to the invention.

The product shown in Fig. 1 is a filler block 1, for instance suitable for locking a housing of a computer C in a box D with a proper fit. The computer C and the box D are schematically represented in broken lines and are mentioned only by way of example. The filler block 1 consists of a body 2 and a number of first 3 and second ribs 4 extending downwards from the body 2. The first 3 and second ribs 4 extend approximately at

right angles to each other. Enclosed between two first ribs 3, two second ribs 4 and the body 4 is a cavity 5 of approximately rectangular cross section. The overall dimensions (length L, width B and height H) of the filler block 1 are large with respect to the amount of material used, and hence with respect to the weight, compared with a comparable solid block of the same material.

The first ribs 3 have a first part 6 which is relatively high with respect to a second part 7 thereof. The second ribs 4 likewise have a first part 8 which is relatively high with respect to the second part 9 thereof. The relatively high parts 6, 8 are arranged together, as are the relatively low parts 7, 9. The low parts 7, 9 thus define an imaginary bottom surface 10. The approximately vertically extending transition parts 11 between the high parts 6 and 8, respectively, and the low parts 7 and 9, respectively, define two imaginary wall surfaces 12 which include an angle with each other and with the bottom surface 10. The bottom surface 10 and the wall surfaces 12 define an imaginary space in which, for instance, a corner of the computer C can be received.

When the computer C is accommodated in a box D, the filler block 1 is received between the computer C and three wall panels of the box D with a proper fit. Preferably, such filler blocks 1 or comparable, suitably shaped filler blocks 1 are fitted between the computer C and the box D at several points, so that the computer C is prevented from shifting and moreover a shock-absorbing capacity is obtained, so that damage is avoided. It is noted that the ribs can be arranged in various orientations and

positions with respect to each other and the body 2, and more or fewer (groups of) ribs can be used. Thus, for instance, the body can be arranged on the side proximal to the product to be accommodated, so that a greater contact surface between the product and the filler block is obtained. In addition, cavities 5 can be open in different directions, or at least locally all or some ribs can extend in one direction only and, for instance, have a meandering, sinusoidal or otherwise bent shape. Further, openings and recesses can be provided in the ribs and/or in the body. These and many other modifications are considered to fall within the scope of the invention.

The filler block according to Fig. 1 is preferably manufactured by injection moulding in a mould as will be further described hereinafter. The manufacture of the filler block 1 will be described starting from a batter S which comprises at least biodegradable polymers. The batter is preferably a solution or suspension, and in particular a suspension of starch or one or more of such natural polymers in water. As will be further described hereinafter, it is also possible to start from a relatively dry starting material, for instance granulate material, and other compositions can also be used. A choice for a batter or, for instance, granulate material, can for instance be made depending on the desired supply means, desired energy consumption, flow paths in the mould and in the feed track, availability of starting materials and the like. In this description, "gelatinization" is intended to refer to a change of a natural polymer from a slightly or completely loose granular or comparable granulate form into a dry or non-dry

and/or foamed cohesive form, in which stretched polymers are present which are mutually bonded to a limited extent only, if at all. That is to say, a transition occurs from a solid substance, a colloidal solution or suspension to a more homogeneous fluid mass.

The batter is liquid at room temperature and slightly above that, at least below the gelatinization temperature of the polymers or at least the greater part thereof, which renders it easy to process, since the suspension has a good flow behaviour and can simply be pumped. This provides the additional advantage that the polymers are not damaged during supply, for instance by an extrusion press screw. Moreover, such a suspension can be manufactured and preserved in a simple manner. A further advantage is that it is entirely biodegradable and that starch is a raw material which is simple to obtain, cheap, and present in abundance, which, moreover, in contrast with, for instance, products based on mineral oil and the like, is continuously replenished. The water at low temperatures serves as solvent or suspending agent and as liquefier and, upon strong heating, as blowing agent. As desired, additives can be added to the suspension, such as for instance emulsifiers, liquefiers, other blowing agents and colouring and flavouring substances. Further, for instance thermoplastic plastics can be added in relatively small amounts, for instance for a further improvement of the strength properties or for a further improvement of the resistance to moisture and temperature influences or to wear.

In an alternative embodiment, the starting material is a substantially dry, granulate-form mass M, which will be further explained hereinafter.

Fig. 2 schematically represents an injection-moulding apparatus for use with a method according to the invention, together with a mould suitable for the manufacture of a product according to Fig. 1.

The injection-moulding apparatus 20 comprises a supply device 21 for a batter S, a spray nozzle 22 and a mould 23. The supply device 21 comprises a cylindrical wall 24 with a plunger 25 movable therein with a proper fit. At a first end the cylindrical wall 24 connects to the spray nozzle 22, and remote from the spray nozzle 22 a supply opening 26 is provided in the wall 24, to which a supply pipe 27 for batter is connected. The batter S is for instance supplied from a storage tank 28 utilizing a pump 29.

The spray nozzle 22 consists of a conically shaped first part 30, tapering in the direction away from the wall 24, and a second part 31, connecting thereto, of circular cross section, which second part 31 is narrow with respect to the cylindrical wall 24. Via a thermally separating connecting piece 32, the second part 31 connects to a gate 33 of the mould 23. Further included are means, not specifically shown in the drawing, for shutting off the supply opening 33, after the introduction of a suitable amount of batter into the mould. These means can for instance be part of a plunger 25 or be formed by valve means or the like. The thermal separation between the supply means and a

mould and the or each product to be formed therein should be maintained by these means.

Provided in the mould 23 are a number of mould cavities 34, which will be further described hereinafter and two of which are depicted. Different numbers of mould cavities can be provided, which are identical or different. The mould cavities 34 are connected to the gate 33 via mould channels 35 (Fig. 2A). Connecting to the or each mould cavity 34 at a point remote from the mouth 36 where the relevant mould channel 35 opens into the mould cavity 34 are one or more deaeration channels 37 which are in communication with the environment. This communication is preferably free, but may also be adapted to be shut off, for instance by a pressure relief valve. The mould 23 is suitably divisible along a plane V which intersects the or each mould cavity, in such a manner that products formed in the or each mould cavity can be simply removed therefrom. Further, for the or each mould cavity 34, withdrawal or eject means 38 may be provided for pushing clear the products formed.

Arranged around the cylindrical wall 24 are means 39 for cooling the batter S. Cooling should herein be understood to mean maintainance at a temperature which is below the temperature at which gelatinization of the natural polymers in the batter occurs. These cooling means can for instance consist of coolant-conveying pipes 39. Such cooling means 39' are likewise arranged around the spray nozzle 22. The mould 23 is entirely and/or locally heated utilizing heating means 40 incorporated therein. The thermally separating connecting piece 32 contributes to a thermal uncoupling of the supply device 21

and the mould 23. Cooling of the section 21, 22 of the apparatus upstream of the mould 23 prevents the occurrence of gelatinization, cross-linkage or chemical change in the suspension in the supply device, which would adversely effect the flow properties thereof in particular.

The mould 23, of which Fig. 2a shows a part with a mould cavity 34 on an enlarged scale, contains different heating means 40. In the exemplary embodiment shown, the mould cavity 34 is defined by a number of slotted recesses 41 intersecting each other approximately at right angles, in a first part 42 of the mould 23, and a trough-shaped hollowing 43 in a second part 44 movable against the first part 42 of the mould. The depth of the hollowing 43 is small with respect to the width and the length thereof; the width of the recesses 41 is small with respect to the depth and the length thereof. When the first part 42 is clamped against the second part 44, the mould cavity defines a space corresponding with the shape of the product according to Fig. 1.

In the projections 45 formed between the recesses 41, a heating element 46 is included, for instance an electric heating element. It is noted that the mould parts can also be heated indirectly. On the side of the hollowing 43 remote from the dividing plane V, likewise heating elements 46 are included. The temperature of the different heating elements is preferably controllable individually, but several or all heating elements may also be coupled. In addition, the mould can be heated externally from one or more sides, for instance electrically or by steam or gas burners. Through the heating elements 46 and

optional other means, the temperature of the mould can be raised in such a manner that in the mould cavity 34 during use, as desired, at all times and at all points the desired high baking temperature is achieved and maintained.

The injection-moulding apparatus according to Figs. 2, 2a can be used as follows.

The mould parts 42, 44 are clamped against each other and the eject means 38, if any, are set in the rearmost position, outside the mould cavity or mould cavities 34. The plunger 25 is moved in the direction away from the spray nozzle 22, beyond the supply opening 26. As a result, the supply opening 26 is cleared and the interior of the supply device 21 and the spray nozzle 22 are filled with batter S. The cooling means 39, 39' and the heating means 40, 46 are switched on in such a manner that the different parts are adjusted to the desired temperature and so maintained. To that end, the temperature can be maintained constant or be varied during the baking and/or cooling time. The plunger 25 is moved forwards over a short distance, so that an amount of batter is pressed into the mould and into the mould cavities 34 under high pressure, whereafter the gate 33 is shut off, under a suitable thermal separation. In the mould cavities 34 the batter is brought to the desired temperature, for instance between 150°C and 250°C, and maintained at that temperature for a "baking time" of, for instance, 2 minutes. As a result, gelatinization and subsequent cross-linking of the (natural) polymers occurs. In addition, the strongly heated water and/or other liquids evaporate from the batter, giving rise to the formation of bubbles. In the batter, bubbles are

formed which are partly encapsulated by the cross-linked structure. This yields a foam structure, which can be further enhanced by adding extra blowing agent. In order to allow substantially all of the evaporating moisture to escape from the mould, a sufficiently large number of vents are provided. After the baking time, the mould 23 is opened in two or more parts and the products are taken from the mould cavities 34 or pushed out of them using the ejectors 38.

Upon heating of the suspension to a temperature above 62°C, and at least above the gas formation or vaporization temperature of the or a blowing agent, within the suspension gelatinization of the starch occurs and moreover bubble formation as a result of evaporation of the water. Upon further heating of the suspension, cross-linking of the polymers occurs, yielding a firm, relatively dense structure around cells that result from the evaporation of the water and optional other blowing agents.

The injection-moulded product has an at least substantially closed skin 13 of closed cells and a foamy core 14 which comprises open cells 15. In Fig. 1a, on an enlarged scale, twice a cross section through one of the ribs 3 is shown, on the left in a highly schematic representation, on the right in a more realistic form. The closed skin 13 provides for a good resistance to external influences, such as for instance moisture and temperature, while the core 14 provides, among other things, for a large volume combined with a relatively small weight and for good resilience. Further, the skin 13 has a rigidity- and strength-enhancing effect. The walls 14', as a result of the baking, have a firm skeleton.

The skin is dimensionally stable and has a smooth and taut appearance, which is esthetically advantageous and moreover enables, for instance, its being printed on, as well as the provision of relief using the or each mould cavity.

As long as the skin 13 remains closed, biodegradation of the product is adequately prevented or at least slowed down to a great extent. Through a suitable choice of the temperature build-up and the pressure build-up in the mould cavity, the properties of the product can be influenced, for instance in that the skin 13 is thinner or thicker with respect to the core 14 and in that the core 14 and the skin 13 are cross-linked to a greater or lesser extent ("well-done"). By variation of the temperature in time and/or in the different parts of the mould, and in particular by changing the temperatures of the different projections 45, the properties of the different parts of the product can be changed, so that, for instance, the elasticity of the parts can be different.

In contrast with the known method in which use is made of platen sets, with injection moulding, first the mould cavity is closed and only then is the batter introduced into the mould. As a consequence, the total volume of the mould cavity can be greater than the volume of the separate mould cavity parts as contained in the mould's first 42 and second part 44, respectively. In fact, in the known method, the batter is to be introduced into a cup-shaped cavity and held therein until the mould is closed. When the mould is being closed, the batter moreover cannot be allowed to be pressed away across the edges because it will then flow between the land areas and prevent

closure of the mould or at least render it more difficult. In the known method, therefore, the total volume of the closed mould cavity should be considerably smaller than the volume of the cup mould, which moreover initially includes all of the moisture which subsequently evaporates.

Fig. 3 shows a cross section of an inner tray 50 in a storage box 51, in which inner tray 50 for instance a household appliance 52 can be accommodated. The inner tray 50 is dish-shaped, that is, at least for the most part thin-walled, and has a receiving cavity 53. Situated adjacent the upper edges 54 of the receiving cavity 53, on opposite sides, is a clamping projection 55 which is formed integrally therewith and has an undercut 56 under which the shaver 52, which is shown in broken lines, can be pressed down. The inner tray has been formed by injection moulding, utilizing a divisible core. As a consequence, the clamping projections 55 can be integrally injection moulded. Accordingly, the method according to the invention also enables the manufacture of biodegradable, non-withdrawable products in one processing pass, which renders such products particularly suitable, for instance, as packaging material, storage material and the like, but also as filling material, for instance for sandwich-shaped construction parts, for housings and the like.

Fig. 4 shows a filler product 60, in the form of a so-called "loose fill material", a filler product 60 which is used for packaging products in a shock-absorbing manner in, for instance, boxes, cases, crates or like packages. To that end, a multiplicity of the filler products 60 are loosely poured into

the space between a product (or products) to be packaged and the package, whereafter the package can be closed and movements of the packaged product within the package are prevented or at least accommodated in a shock-absorbing manner. To that end, the loose fill material is slightly elastically deformable.

The filler product 60 as shown in Fig. 4 comprises an approximately cylindrical core 61 and a number of fins 62 extending approximately radially from the core, and which extend throughout the length of the core. The fins are relatively thin with respect of their height and length, so that they exhibit a measure of bending slackness. The circumference of the filler product 60, measured along the tops of the fins 62, is largely determinative of the volume the filler product occupies, so that a favourable volume-to-weight ratio is obtained.

The filler products according to Fig. 4 and similar for instance lengthwise symmetrical products can be formed by extrusion on an apparatus according to Fig. 5. The extrusion apparatus comprises a supply device comprising means 80 for the (semi)continuous pressurized supply of batter S for a granulate-form mass M, whether or not pre-foamed to some extent, from a storage tank to a spray nozzle 81, for instance utilizing one or more pumps. Connecting to the spray nozzle 81 in this extrusion apparatus is an extrusion die 63 which comprises one or more extrusion orifices 64 of a cross section which substantially corresponds to, at least is similar in shape to, the cross section of the filler products to be obtained. The supply device 80, and in particular the spray nozzle 81 are provided with cooling means 82, for instance as described in the foregoing.

The extrusion die comprises heating means 65 which are arranged in such a manner that at least in the extrusion orifices the temperature can be accurately controlled, for instance to 150° to 200°C. Arranged on the side of the extrusion die 63 remote from the supply device 80 is a cutter 66 by which extruded sections can be cut into short lengths upon exiting from the extrusion orifices.

The apparatus according to Fig. 5 can be used as follows.

From the supply device 80, a continuous flow of batter S or a mass M in granulate form, whether or not in a slightly pre-foamed condition, is fed via the spray nozzle 81 to the heated extrusion die 63 and forced through the or each extrusion orifice 64. The leading part of the batter gelatinizes and proceeds to cross-link, whereby the moisture evaporates from the batter and provides for the foaming of the product, optionally together with additional blowing agents and other additives. Preferably, the cross section of the or each extrusion orifice 64 widens slightly in the direction of extrusion, in such a manner that during the foaming of a product, as the baking batter S is being passed through the extrusion orifice, the pressure that is exerted on the filler product 60 is sufficient to obtain the desired skin and core properties, without the cross-linked structure thereof being broken or otherwise damaged by the extrusion die.

As a result of the continuous supply of batter, the "baked" part of the extruded section is pushed forward, in such a manner that it leaves the corresponding extrusion orifice 64. On the leading side, each time a part of the section is cut off,

whereby the cut surface is closed. In this manner, at a relatively high rate and at relatively low cost a large amount of loose fill material can be manufactured from a liquid batter. These filler products are biodegradable or sections in great lengths, and may also be in sheet form, for instance.

When the batter is liquid, preferably in the form of a solution or suspension, manufacture, storage, transport and dosage thereof are particularly simple and in a method according to the invention use can be made of a simple apparatus, which renders these methods relatively cheap. Further, in most embodiments the natural polymers need not be subjected to any expensive pretreatments before they can be used. They only need to be included in the batter.

In the foregoing, methods and apparatuses have been described for manufacturing biodegradable products with a foamed structure using an injection-moulding technique and an extrusion technique, the starting material being a liquid batter, in particular a solution or suspension. However, as indicated, it is also possible to start from a substantially dry mass consisting of, or at least comprising, for instance, a granulate material. The granulate material can, for instance, comprise more or less spherical particles having small dimensions with respect to the orifices in the moulds and supply means. Like a liquid, these particles can display a certain flow behaviour, as a result of which, under pressure of the supply means, they can fill the mould or be conveyed through it.

The particles which can contain, for instance, water or a different blowing agent in relatively small amounts, are heated

after being introduced into the mould and will swell as a result, since the blowing agent present will blow up the particles, just as in the case of the particles included in the solution or suspension. With such a starting mass too, the polymers will provide for a high degree of cross-linkage and hence a firm cell wall of the blown cells. It is true of such a method too, that the mould as hot part together with the pressure and the blowing agent will lead to a high degree of densification of the outer parts of the walls of a product, the so-called skin, while the core will contain larger cells.

Due to the fact that in this method less moisture is included in the starting mass, relatively little energy is necessary therefor, in that less heat is needed for the evaporation. This is precisely what is of particular importance for the manufacture of biodegradable products, in view of the environmental advantages that can be achieved with such products. Partly as a consequence of relatively cheap raw materials and high production rates that can be achieved, thus a low-energy, environment-friendly and economically advantageous production method has been obtained for products that present few environmental problems, if any, also in the downstream stage, that is, as waste.

When a mass M in granulate form is used, of course a different flow behaviour occurs than if a batter S is used. Moreover, not every starting material is suitable for use as or in granulate form, at least not advantageously so. Moreover, when using granulate material together with fillers, or combinations of granulate materials, it is sometimes not easy to

prevent separation or to obtain and/or to maintain a good constant mixing.

For that reason too, products according to the invention are practical for use as packaging material, while moreover they do not present any problems regarding static charge.

In order to improve the appearance of the products, a colorant can be added to the batter or a surface layer can be formed, for instance through texture differences or by variation in temperature of the mould at different positions across the surface, so that local changes occur in the skin as a result of different baking conditions. Naturally, it is also possible, after manufacture, to provide parts of the product with a coating, coloration or printing. Furthermore, it is possible to mould in, for instance, inserts in the product.

By way of illustration, examples are given of methods according to the invention, which should not be construed as being limitative in any way.

Example I

1000 g potato starch was introduced into a Hobart mixer and under stirring at low speed (position 1) successively 2 g Kelzan S, 2 g hydroxyl apatite, 75 g China clay Spes and 75 g Hydrocarb 90 were added thereto. After all components had been added, mixing occurred for another 15 minutes (position 1). This mixture was introduced into a priorly measured and stirred composition of 1150 g mains water and 22 g silicone HY oil. After all components had been stirred (position 2) to form a

liquid batter, this was introduced into a supply device of an adapted injection-moulding machine. The injection-moulding machine used is of the type EPS-10, of the firm Thermoware of Barneveld. The injection-moulding machine used comprised a mould with ten mould cavities for forming trays, each tray having a size of 150 * 75 * 25 mm (L * B * H) and a wall thickness of 2.5 mm. The injection mould comprised electric heating elements and a plunger-injection device with a shut-off thermally uncoupled from the mould. Per mould cavity, approximately 15 cc batter was injected under a pressure of 2 bar and at a temperature of 20°C. The mould was heated to 210°C, with a temperature tolerance of between 200°C and 220°C and the mould was closed with a force of 5 kN per mould cavity. The mould was closed for 120 s and maintained at the required temperature, so that each mould cavity was filled entirely with foamed product. During heating, 98% of the water escaped, substantially in the form of vapour, via vents in the mould, with the water functioning as blowing agent. After 120 s the mould was opened and the injection-moulded products were pressed from the mould cavities using the ejectors. The thus formed products were directly ready for use. Each product had a core of a thickness of approximately 2.1 mm, covered on opposite sides by a skin of a thickness of approximately 0.2 mm. Each product had a moisture content of approximately 1% and a weight of 8 g.

Example II

A batter was prepared in the same manner as in Example I. At a pressure of 4 bar, this batter was continuously fed to an extrusion die with a star-shaped orifice of a cross section of 250 mm^2 and a length of 50 mm, which aperture was 150 mm long in the downstream direction. The die was heated to a temperature of 210°, so that approximately 95% of the water evaporated from the batter to form cells, while in the batter gelatinization and cross-linkage of the starch polymers around the cells occurred. Upon leaving the die, a section had been formed with a foam core, covered by a skin of a thickness of approximately 0.1 mm, the product formed being pushed out of the die by the batter being introduced. The thus formed section had a specific weight of approximately 150 g per dm^3 and could simply be cut into short lengths for the formation of loose fill material.

Example III

An amount of native starch in granulate form is introduced into a pretreatment apparatus. The granules have approximately a spherical shape with an average diameter of approximately 50 µm, each granule having a water content of approximately 20%. The granulate material is adjusted to a slightly increased temperature, whereafter a reduced pressure is provided for, in such a manner that the granules are prefoamed. During prefoaming the granules acquire a diameter of approximately 100 - 150 µm, while the water content decreases to approximately 10%. Using a pneumatic plunger system, 85 cc prefoamed granulate material with a density of approximately 100 - 180 g/l is forced into an

injection mould. The injection mould has a trough-shaped cavity having the dimensions 190 * 125* 18 mm with a wall thickness of 3 mm. The mould is kept closed with a force of approximately 5 kN per cavity and is subsequently heated to approximately 200°C for approximately 40 s, which results in gelatinization and cross-linkage of the natural polymers, while the water substantially evaporates from the granules, giving rise to further foaming. The wall of the thus baked product has a core of open, blown and relatively large cells, while the outsides of the wall have a structure of compact, relatively small and substantially closed cells. The thus obtained tray is thereupon taken from the mould, is then dimensionally stable and has a water content of approximately 1%.

The invention is not in any way limited to the embodiments shown or described. Many variations are possible. The freedom of design which can be achieved with the methods according to the invention is virtually unlimited. Thus all kinds of other products can be manufactured with a method according to the invention, such as for instance trays for chips or snacks, edible containers such as ice-cream cups, sheet, bar and profiled material for all kinds of uses and many other comparable substantially thin-walled products. These and comparable variations are understood to fall within the scope of the invention.

CLAIMS

1. A method for manufacturing biodegradable products with a blown foamy structure, wherein a mass comprising at least natural polymers such as starch is passed under pressure into or through a mould (23, 63) and the mass (M, S) is heated in the mould (23, 63) in a manner such as to give rise to at least cross-linking of natural polymers, while the mass prior to the introduction into the mould has a temperature which is below the gelatinization temperature and in the mould is brought at least to the baking temperature.

2. A method according to claim 1, wherein the cells (15) substantially have a wall of natural polymers cross-linked during heating, while the cell size across the wall thickness of each product is varied, in such a manner that it decreases in outward direction (Fig. 1a).

3. A method according to claim 1 or 2, wherein each product is formed with a number of sheet, bar or dish-shaped parts (2, 3, 4; 50; 61, 62) each having in at least one direction a dimension that is relatively small with respect to the total dimensions of the product (1; 50; 60).

4. A method according to any one of the preceding claims, wherein the mass is formed by a liquid batter, comprising a suspension or solution (S) of at least the natural polymers such as starch in a liquid.

5. A method according to claim 4, wherein a batter (S) is used which consists substantially entirely of biodegradable constituents.

6. A method according to any one of the preceding claims, wherein a batter of at least water and starch is used and the mould is heated to a temperature of more than 130°C, and preferably between 150°C and 200°C.

7. A method according to any one of claims 1-3, wherein the mass is introduced into the mould in a relatively dry condition, preferably in granulate form.

8. A method according to claim 7, characterized in that the mass prior to the introduction into the mould is slightly prefoamed without this giving rise to gelatinization.

9. A method according to any one of the preceding claims, wherein a blowing agent, preferably at least water, is included in the mass (M,S).

10. A method according to any one of the preceding claims, wherein as mould an injection mould (23) is used.

11. A method according to any one of claims 1-7, characterized in that as mould an extrusion die (63) is used.

12. A method according to any one of the preceding claims, wherein the product is baked in the mould.

13. An apparatus for manufacturing biodegradable products (1, 50, 60), comprising a mould (23, 63) which contains at least one mould cavity (34, 64) and supply means (20, 80) for feeding a mass (-) under pressure into the or each mould cavity (34, 64), wherein heating means (40, 46; 65) are provided for heating the mould and wherein means (32; 39, 39', 82) are provided for keeping the supply means relatively cool with respect to the mould, in such a manner that the mass disposed therein is maintained at least below the gelatinization temperature.

14. An apparatus for manufacturing biodegradable products (60), comprising an extrusion die (63) which comprises at least one extrusion orifice (64) and supply means (80, 81) for feeding a mass (M,S) under pressure into and through the or each extrusion orifice (64), wherein heating means (65) are provided for heating the die (64) and wherein means (82) are provided for keeping the supply means relatively cool with respect to the die, in such a manner that the mass disposed therein is maintained at least below the gelatinization temperature.

15. An apparatus according to claim 13 or 14, wherein the supply means (20, 60) for the mass (M,S) to the mould or die (23, 63) comprise pumping means.

16. An apparatus according to any one of claims 13-15, wherein the heating means (46) comprise channels in the mould or die for passing therethrough a heated fluid, for instance steam or oil.

17. An apparatus according to any one of claims 13-16, wherein the heating means comprise electric heating elements (46), for instance heating coils or induction heating means.

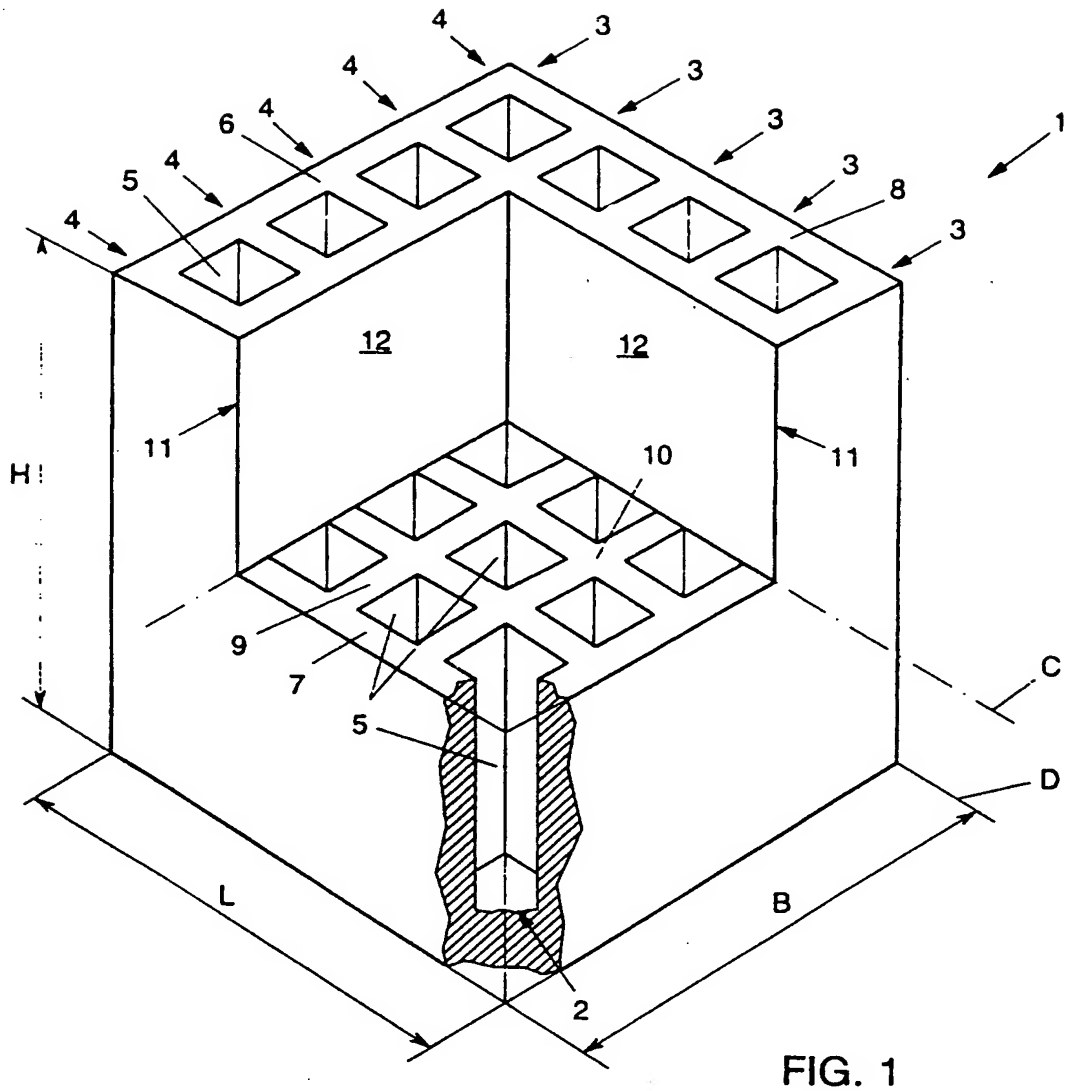

FIG. 1

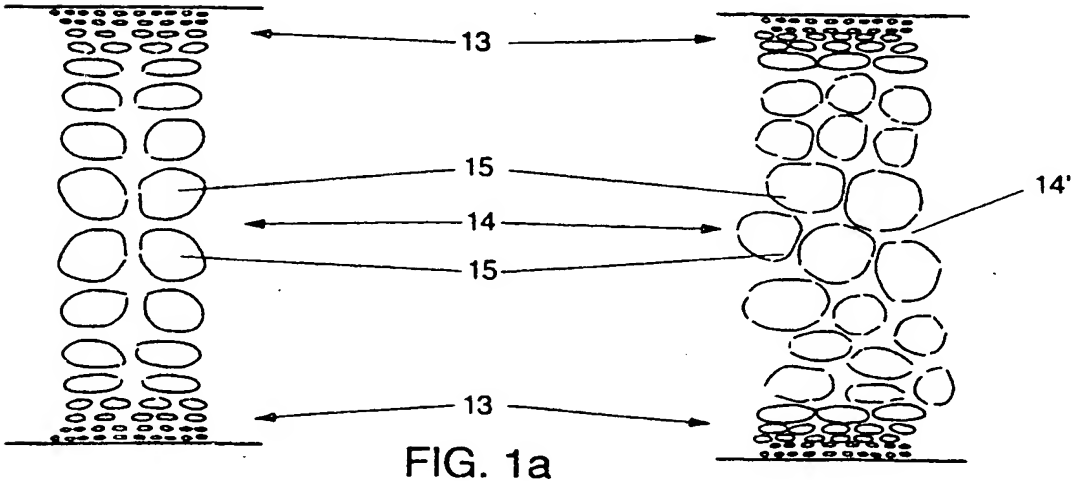

FIG. 1a

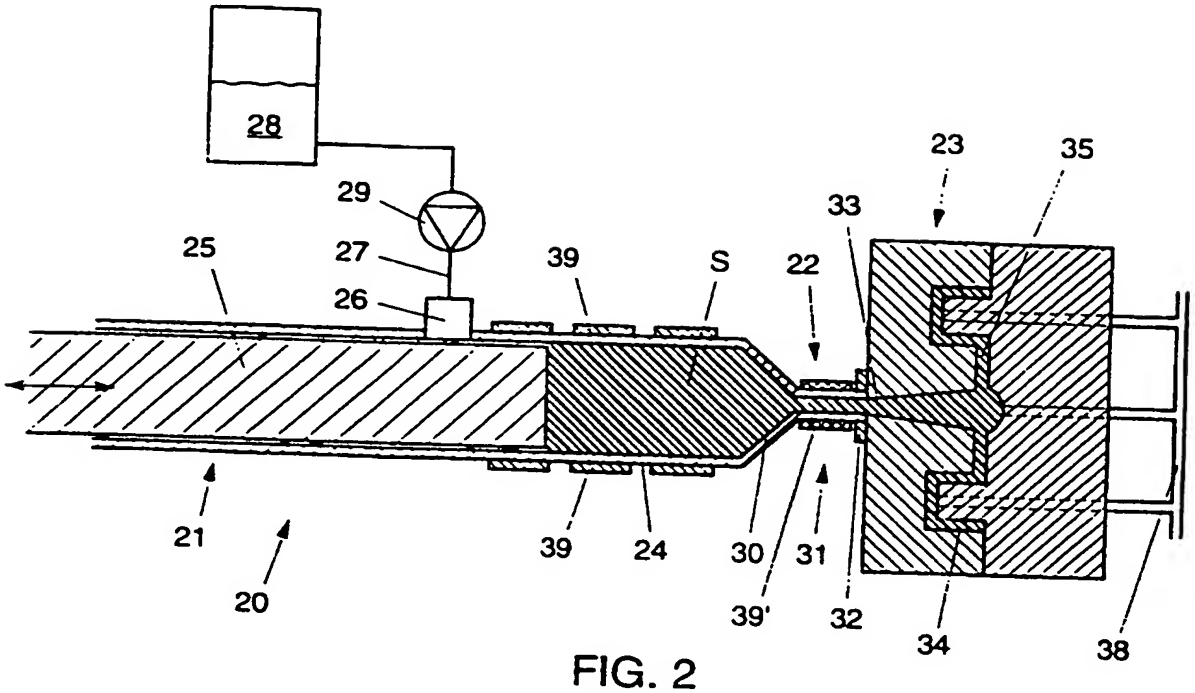
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FIG. 2

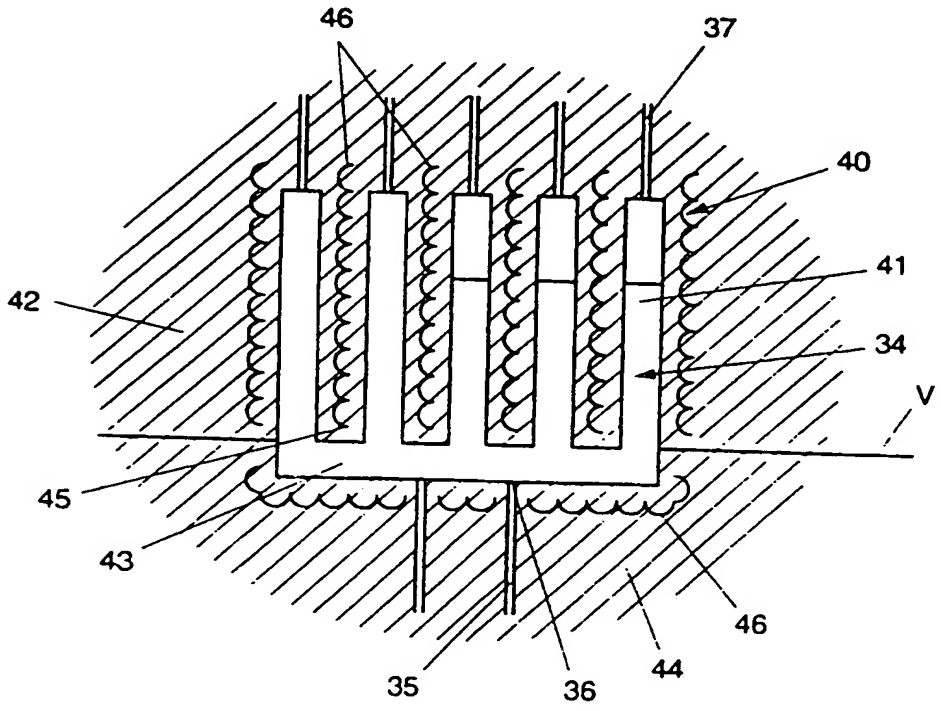
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FIG. 2a

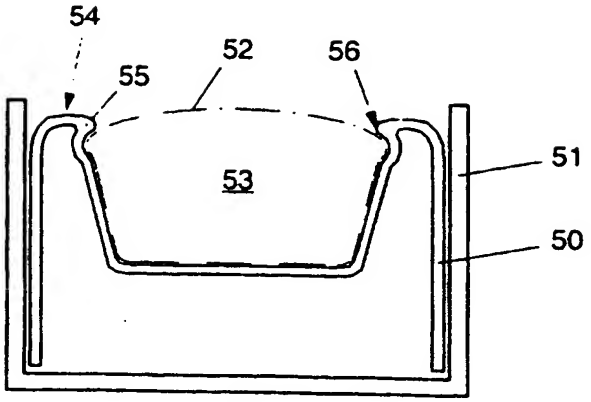

FIG. 3

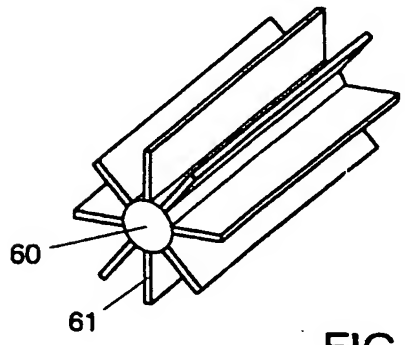

FIG. 4

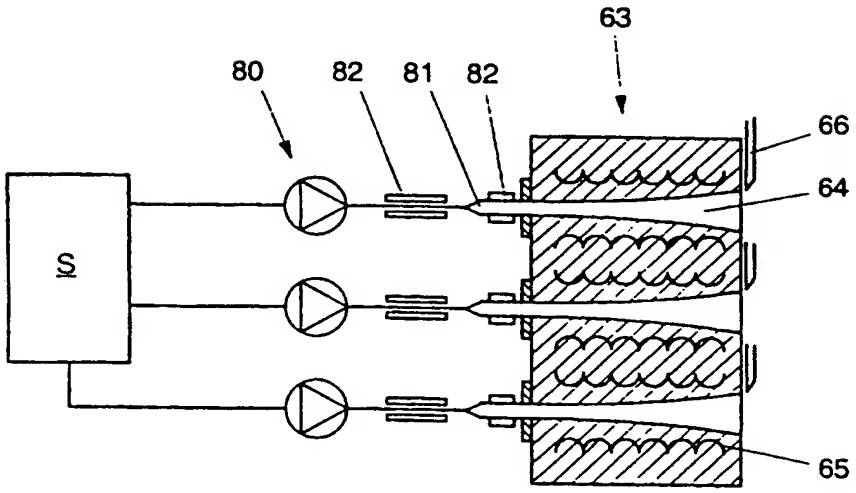

FIG. 5

INTERNATIONAL SEARCH REPORT

I. tional Application No
PCT/NL 96/00136

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C44/34 C08J9/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,95 04104 (BIO TEC BIOLOG NATURVERPACKUNG ;TOMKA IVAN (CH)) 9 February 1995 cited in the application see page 11, line 6 - line 28 ---	1,3-17
X	WO,A,92 13004 (CMI CAPITAL MARKETING INVEST) 6 August 1992 cited in the application see page 22, line 7 - line 23 see page 26, line 22 - page 27, line 17 see page 44, line 5 - page 46, line 36 see page 49, line 1 - line 9; figure 5 ---	1,3-17
A	EP,A,0 634 261 (SUZUKI SOGYO KK) 18 January 1995 cited in the application see page 17, line 33 - line 40; figure 19 --- -/--	3,13

[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 June 1996	21.06.96

Name and mailing address of the ISA	Authorized officer
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Form PCT ISA.210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 96/00136

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 186 990 (STARCEVICH BRADLEY K) 16 February 1993 see column 2, line 11 - line 13 see column 4, line 17 - line 19; figure 2	3,14
A	EP,A,0 587 078 (NIPPON SYNTHETIC CHEM IND) 16 March 1994 see examples 11-13,16-18	1-17
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